

DATA EVALUATION RECORD

CHEM 053201

STUDY 6
Methyl Bromide

FORMULATION--90--FORMULATION NOT IDENTIFIED

STUDY ID: ^{ACC.} 258932 *MRID 00152338*
Dally, L. and J. Rowe. 1985. California methyl bromide sampling study. Unpublished study received on July 26, 1985, under 5785-4. Prepared by Golden Associates and submitted by Great Lakes Chemical Company.

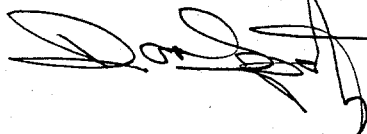
STUDY ID: ^{ACC.} 258931 *MRID 00152337*
Lozier, W.B. and J.E. Baker. 1985. Florida methyl bromide sampling study. Unpublished study received on July 26, 1985, under 5785-4. Prepared by Golden Associates and submitted by Great Lakes Chemical Company.

DIRECT REVIEW TIME = 4

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AUG 15 1990

This study was previously reviewed by Dynamac in 1986. A copy of the review is included in this document because it provides useful information for the ground water assessment; the study was not reevaluated because no new information has been provided to date in response to the previous review.

CONCLUSIONS:

Ancillary Study - Ground Water Monitoring

1. This monitoring study is scientifically valid. Complete treatment history for the wells was not provided. Therefore, the value of this study towards evaluation of the potential for methyl bromide to contaminate ground water is limited.



2. Methyl bromide and trihalomethane were not detected (<1 and 10 ppb, respectively) in water samples from domestic and irrigation wells located throughout California (12 wells) and Florida (19 wells). In California, the sampled wells were located less than or equal to 400 yards from fields with a 10-20 year history of annual methyl bromide use that had been treated with methyl bromide 4-17 months prior to sampling (no treatment history provided for Florida).

METHODOLOGY:

Domestic and irrigation wells (10- to 270-foot depths) located throughout California (12 wells total in Tulare, Fresno, and Monterey Counties) and Florida (19 wells total in Gadsden, Dade, Palm Beach, Collier, Highlands, Manatee, and Hillsborough Counties) were sampled in January or March, 1985, to assess the potential for ground water contamination from methyl bromide. The wells in California were adjacent (less than or equal to 400 yards when reported) to fields with a 10-20 year history of annual methyl bromide applications and which had been treated most recently 4-17 months prior to sampling (no treatment history was reported for the Florida wells). Water samples were either collected from a spigot, bailed with a stainless steel bailer, or obtained from a discharge line. Two water samples were collected from each well into sterilized glass vials. The pH and temperature of the water were measured at the time of sampling.

Water samples were analyzed for methyl bromide and trihalomethane using GC/MS within 15 days of collection. The detection limits were 1 ppb for methyl bromide and 10 ppb for trihalomethane.

DATA SUMMARY:

Neither methyl bromide nor trihalomethane were detected (<1 and 10 ppb, respectively) in the well water samples from California and Florida.

At the time of sampling, the temperature of the water ranged from 15 to 25°C and the pH from 5.3 to 8.0.

COMMENTS:

1. The treatment history for the Florida wells was not provided; although the table of contents referred to a table describing the wells, this table was omitted from the hardcopy received to review.
2. The researchers reported that the concentrations of methyl bromide in water samples fortified with methyl bromide decreased by 18% over a ten-day period, regardless of whether the samples were refrigerated or stored at room temperature. This decrease was not expected to have affected the results of the study.

DATA EVALUATION RECORD
DATA CALL-IN

CASE GS DISC 30 TOPIC GUIDELINE 40 CFR 161-1

CHEM METHYL BROMIDE

BRANCH EAB DISC--

FORMULATION 00-ACTIVE INGREDIENT

FICHE/MASTER ID NO FICHE CONTENT CAT -- 01

A hydrolysis study with methyl bromide. Study No. Will - 49003.
Research Report, Analytical 85:1, Jan.13, 1984. Unpublished report
Submitted by Great Lakes Chemical Corp. Acc. No. 257447.

SUBST. CLASS =

DIRECT RVW TIME = (MH) START-DATE END DATE

REVIEWED BY: Hudson L. Boyd
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8/7/85

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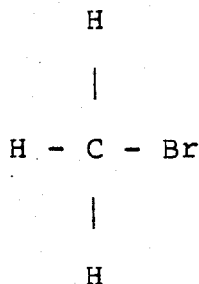
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DATE:

CONCLUSION:

1. This study is scientifically valid.
2. Methyl bromide hydrolyses to methanol, inorganic bromide, and two unknown components, principally the first two at an average rate of 1.4mg methyl bromide /litre of H₂O/day at 25 C. Apparently hydrolysis is not pH dependent at 25 C.

3. This study partially fulfills EPA Data Requirements for Registering Pesticides (1983) by providing data on the hydrolysis of methyl bromide per Guidelines Section 161-1.



BROMOMETHANE, METHYL BROMIDE

MATERIALS AND METHODS

Three experiments were set up to follow the hydrolysis of methyl bromide (MBr) at either pH 5, 7 or 9. Each experiment utilized a series of 500 ml (actually 555ml) Erlenmeyer flasks equipped with screw caps modified with holes into which were fitted Teflon liners which served as septa. By means of the septa MBr could be added and samples removed from the flasks without removing the caps. Flasks, caps, buffer and measuring cylinders were sterilized by autoclaving; hydrolysis of MBr at about 70-100 ppm in the buffer was followed.

pH 5 buffer (actually pH 4.90) was prepared with sodium acetate, water, and glacial acetic acid. Buffer of approximately pH 7 was also prepared with acetate and measured to be pH 6.90. pH 9 buffer (actually pH 8.85) was prepared with anhydrous dipotassium phosphate and water. As stated, each buffer was sterilized by autoclaving prior to use.

A primary MBr standard was prepared from Linde gas of 99.5% purity by transferring 1.0 ml MBr through the septum into a 4320 ml bottle filled with air (conc = 981 ng/ml air). By means of an air tight syringe 5.0 ml of this primary standard was transferred to one of the Erlenmeyer flasks (conc = 8.84 ng/ml air). This flask then contained a working standard of MBr.

A standard of methane (from house line) in methanol, HPLC grade, (conc = 0.25 ug/ml) was prepared daily.

Acidic acetonitrile was prepared by adding 15 ml of 0.6N H_2SO_4 to 75 ml $\text{C}_2\text{H}_3\text{N}$ in a separator and adding 5 g $(\text{NH}_4)_2\text{SO}_4$, removing the upper phase and drying it with anhydrous sodium sulfate. Sufficient volumes of this acetic acetonitrile were added to 2-bromoethanol to prepare a working standard of the latter (conc = 0.88 ug/ml).

Ethylene oxide was added to 96 ml acetonitrile to bring the volume to 100 ml. This solution was prepared daily.

On each day of analysis chromatography of standard solutions was checked on each chromatograph; resultant chromatograms were considered to be raw data. Two types of samples (known volumes from headspace and aqueous solutions diluted with MeOH) were analyzed by gas chromatography.

In preliminary work similar responses were obtained with either air or liquid samples containing MBr so standards prepared in air were used to quantitate all analyses. Varian Model 3700 with ^{63}Ni EC detector, a glass column (2 m x 2 mmid) packed with 10% Carbowax 20M on Chromasorb WHP was used. Carrier gas was high purity N with a flow rate of 30 cc/min. Column oven, injector and detector temperatures were 60°, 150°, and 340°C respectively. MBr retention time was about 0.4 min.

Inorganic bromide (iBr) was determined by the method of Heuser and Scudamore (1970) in which the iBr was reacted with ethylene oxide to produce 2-bromoethanol which was then measured quantitatively by gas chromatography. For these analyses, the instrument was a Tracor Model 222 with a ^{63}Ni EC detector. The column was packed as mentioned before with 10% Carbowax 20M on Chromosorb WHP 80/100. Again the carrier gas was nitrogen but the oven, injector and detector temperatures were 140°, 150° and 325°C respectively. The retention time for bromoethanol was about 2.1 min. 5 ul aliquots of unknown isolates and standard solutions were chromatographed - acetic acetonitrile was used as a diluent as required.

Following the analysis for MBr a second procedure was followed to determine whether or not there were degradates such as methane and methanol which might not be detected by electron capture but might be detected by a flame ionization detector (FID). For these analyses a Varian 3700 with FID and a glass column (2m x 2mmid) packed with 3% SP-1500 on 80/120 Carbopak B. (Supelco) was used. High purity N at a flow rate of 20 cc/min and detector air and hydrogen at 300 cc/min and 30 cc/min, respectively, were also used. Column oven, injector, and detector temperatures were 100°, 150°, and 340°C and methane and methanol retention times of about 0.6 and 0.9 min were experienced.

EXPERIMENTAL

As previously stated, the hydrolysis of MBr was followed at either pH 5, 7, or 9, utilizing a series of flasks from which samples could be removed from the headspaces without opening the flasks. Experiments were run under sterile conditions and the hydrolysis of MBr was followed at a concentration of about 70-100 ppm in the buffer.

MBr was bubbled through the proper buffer, diluted, and analyzed. Additional flasks were set up to contain buffer only. All flasks were stored in the dark at either 25°C or 35°C. At selected times over a 30-day period individual flasks were removed from storage and analyzed as follows:

- 1) A sample was removed from the headspace through the septum and analyzed for MBr and degradants.
- 2) A second sample was removed as described and analyzed for methane, methanol, and degradants.
- 3) The flask was opened and a sample of the buffer was removed and analyzed for MBr and degradants.
- 4) A second sample of the buffer solution was analyzed for methanol and other degradants.
- 5) A third sample from the buffer solution was analyzed for iBr. Solutions from control flasks were analyzed for iBr only. Amounts of components in the headspace and the solutions were calculated as well as the total amounts in each flask.

Another experiment was conducted to determine possible losses of MBr from flasks by diffusion. For this, a series of flasks containing only air were closed and a measured amount of MBr was added through the septum of each flask. At intervals, samples of air were removed and analyzed for MBr.

RESULTS:

At all three pH conditions MBr was found to be present in the headspace of individual flasks. Apparently MBr diffused from the buffer into the headspace(s). Some flasks contained more MBr than those sampled earlier, indicating diffusion from headspace through or around the septa.

Based upon a decrease in MBr at all pH conditions and at both temperatures with concurrent increase in amounts of iBr and appearance of MeOH it was evident that hydrolysis occurred in all cases. Less MBr remained in flasks after 30 days at 35°C than at 25°C. Confirmation of the loss of MBr by diffusion was made by the analysis of samples from flasks containing only air and MBr. When the concentration reached about 6 mg/flask it appeared that equilibrium had been established. It was clear that the best criterion for judging hydrolysis was in the increase in formation of iBr which was almost linear with time for the first 10 days. Rates were calculated from values obtained over the first 4 days; at 25° C it did not appear that hydrolysis was pH dependent and an average was 1.4 mg MBr/litre of water/day. At 35°C rates appeared to be 3 to 5 times higher and there was a suggestion that the rate at pH 5 might be slower than at pH 7 or 9.

DISCUSSION

1. Although it was clear that extensive degradation of MBr occurred by hydrolysis under the three aqueous pH conditions of the experiments, the complexity of the activities and the volatility of MBr precluded precise calculations of rates of hydrolysis. The following activities were occurring:
 - a. diffusion of MBr from the aqueous solutions to the headspace(s).
 - b. diffusion of MBr from the headspace(s) out of the flasks, either around the seals or through the septa.
 - c. hydrolysis, producing methanol and iBr in the solutions.
2. Although data produced were variable, lending confusion in their interpretation, each data point represented only one flask. This tended to correct for the variability resulting from diffusion.